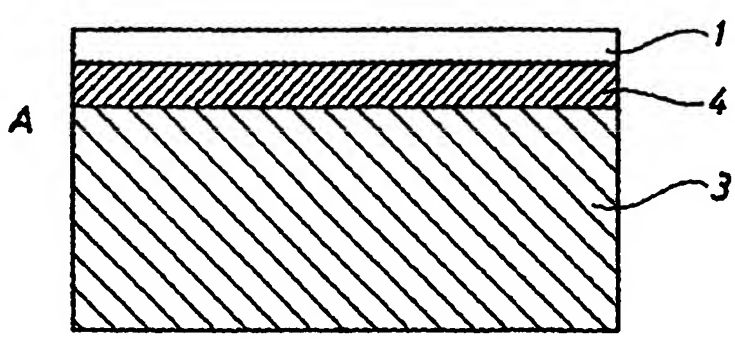




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(54) Title: ELECTROCHEMICAL CELL <div style="text-align: center;">  </div> (57) Abstract <p>Solid oxide fuel cell comprising a porous carrying electrode structure (3) with an electrolyte and yet another electrode applied thereon, where the carrying electrode structure (3) and the electrolyte (1) are sintered together. The known fuel cells are operated at approximately 1000 °C. However, it is desired to go as low as 700 to 850 °C. The latter is encumbered with the draw-back that the characteristic resistance of the electrolyte (1) is increased, which has necessitated a reduction of the electrolyte thickness to approximately 10 to 15 µm. Then the anode is instead the carrier layer. The electrolyte (1) can be tape cast or sprayed onto the anode. However, the finished product must be plane, which according to the invention is obtained by the carrying electrode structure and the electrolyte being manufactured directly atop one another without involving an assembling process prior to the sintering, by the thickness of the carrying electrode structure (3) being less than 700 µm, and by the thickness of the electrolyte (1) positioned thereon being less than 40 µm, whereby a contraction-controlling substance, if desired, is added to the carrying electrode structure. The entire structure can thus be manufactured in one process by way of sintering at 1250 to 1400 °C. As a result a half-cell is obtained which is sturdy and presents a high efficiency, a low waste percentage during the manufacture as well as a reduced material consumption, and which in addition is scalable. In other words an independent half-cell is obtained which is particularly suited for mass production in large dimensions.</p>		

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Title: Electrochemical cellTechnical Field

The invention relates to an electrochemical cell, such as a fuel cell, and comprising a porous, carrying electrode structure, optionally including several layers, on which
5 an electrolyte and another electrode are deposited, where the carrying electrode structure and the electrolyte are sintered together, for instance an Ni/YSZ anode including several layers and where a YSZ electrolyte and a cathode are deposited thereon.

Background Art

10 Such an electrochemical cell with an oxygen-ionic conducting, gasproof electrolyte can be driven as a fuel cell, as fed reducing and oxidizing gases are caused to provide an electrical current to be utilized. As an alternative, the cell can be operated by a power causing oxygen to be removed from the gas at one electrode and fed to the gas at the other electrode. As a result for instance water can be electrolysed on the first
15 electrode, and/or oxygen can be accumulated on the second electrode. Finally, the oxygen fed to the second electrode can be caused to react with the present gas.

The efficiency of the fuel cell can be restricted inter alia by the conductivity and thickness of the electrolyte. Therefore the efficiency and the output of the cells can be improved by minimizing the thickness of the electrolyte. In addition, the electro-
20 lyte has usually been the structurally carrying component of the cell, and therefore a typical electrolyte thickness of 100 to 200 μm has been used. The thickness of the electrodes is typically 20 to 100 μm . The minimizing of the electrolyte thickness is particularly important at low operational temperatures, such as 700 to 850°C.

The basic requirements to the electrolyte are inter alia gas density without through

pores as well as a high conductivity, and accordingly a predetermined purity of the material is required. It is assumed that the electrodes are preferably porous whereby the access for gases to and from the active centres inside the electrode are not reduced by diffusion barriers. The entire cell including an electrolyte and two electrodes must be reasonably plane and of a uniform thickness in order to be stacked in a series connection of cells, a so-called stack. In addition, each cell must be sufficiently strong for tolerating handling and mounting procedures.

The manufacture of a structurally carrying component of a material like the material of an electrode ensures a high degree of freedom with respect to the thickness of the electrolyte. The hitherto known carrying electrode structures are of a thickness of 0.7 to 2 mm. Such a structure is to a certain degree encumbered with draw-backs both with respect to the amount of material used and with respect to the restricted gas flow through the porous structure, viz. the diffusion barrier.

It is possible to deposit an optionally thin or thick electrolyte on a sintered carrier structure by relatively cost-intensive and/or difficult, scalable processes, such as CVD-EVD and plasma processes, which do not require a subsequent sintering of the electrolyte layer.

However, inexpensive wet ceramic techniques for applying the electrolyte layer imply that the carrier structure must be non-sintered or only partially sintered because otherwise it is difficult to subject the electrolyte layer to a dense sintering.

It is possible to manufacture films of the electrolyte material and the carrier structure material on the basis of a slurry of particles (a slip) by inexpensive, scalable and wet ceramic processes, such as film casting, viz. tape casting. These films can be cast directly atop one another or separately and be laminated by way of rolling. Subsequently, the two layers must be sintered together.

If the carrier structure and the electrolyte do not substantially shrink to the same extent during the sintering, stresses arise in the entire material and cause deformations. Therefore it is very important to adjust the shrinkage during the sintering of the two structures. The latter is complicated by the fact that the electrolyte must be gasproof as mentioned above whereas the carrier structure must be porous. According to EP 588 632 the particle layer can be subjected to a dense sintering without involving formation of pinholes provided said particle layer is so thick that after the sintering it forms an electrolyte of a thickness of more than approximately 40 μm . When air bobbles are captured in the slip for instance due to formation of skin during the drying, errors arise in the particle layer, and when said particle layer is not thicker than said error, pinholes may arise.

In addition, the difference in the thermal coefficients of expansion of the two structures, viz. the electrolyte and the carrier structure, plays a role in determining how thick the electrolyte layer can be relative to the carrier structure without inducing too high stresses in said layer. The thicker the electrolyte layer is made the higher stresses arise in the structure during the cooling following the sintering. These stresses can cause crackles in the electrolyte with the result that said electrolyte is no longer gasproof. The situation can be further complicated by the presence of an intermediate electrode structure.

When the electrolyte layer is made very thin, such as less than 10 μm , a risk is, however, involved of the electronic conductivity of said electrolyte being increased by the diffusion therein especially of Mn from the cathode side. An increase of the electronic conductivity corresponds to a short-circuit and is damaging to the fuel cell. Moreover it is known that cations can be repositioned in the electrolyte structure during the passage of an electric current. The latter can affect the conductivity of the material, and the problem is increased proportional to a decreasing electrolyte thickness because the potential gradient is accordingly increased. The latter is in particular to be seen in the light of an expected operation period of 40 to 50,000 hours. In

order to avoid sintering errors and through pores in very thin electrolytes, extreme requirements are in addition presented to a perfect particle packing in the layer which is to form the electrolyte.

Brief Description of the Invention

- 5 The object of the invention is to show how it is possible in a very cost-effective manner to manufacture a structure with a carrier structure and an electrolyte presenting the required properties. By a controlled composition of the materials forming part of the carrier structure it is possible to manufacture a gasproof, thin electrolyte on a carrier structure by way of simple and cost-effective processes suited for mass
10 production. The articles produced must furthermore present a sufficient porosity in the carrier structure and a gasproof electrolyte, be plane without crackles and in addition be very sturdy.

- An electrochemical cell of the above type is according to the invention characterised in that the carrier electrode structure and the electrolyte are manufactured directly
15 atop one another without involving an assembling process prior to the sintering, that the thickness of the carrier structure is less than 700 μm , preferably less than 500 μm and especially less than 300 μm , and that the thickness of the electrolyte deposited thereon is between 10 and 40 μm , preferably between 10 and 25 μm and especially between 15 and 25 μm , as a sintering-promoting substance and an air-entraining
20 substance as well as a contraction-controlling substance can be added to the carrier structure. The entire resulting structure can be manufactured without assembling steps by way of sintering at 1250 to 1400°C. As a result a half-cell is obtained which can be manufactured in one process, is sturdy and presents a high efficiency, a low waste percentage during the manufacture as well as a reduced material consumption,
25 and which in addition is scalable. In other words an independent half-cell is obtained which is particularly suited for mass production in large dimensions. The sintering together, viz. the sintering of the electrolyte layer and the permanent carrier structure

with said electrolyte layer deposited on the carrier structure, implies in addition that a particle packing is obtained which is sufficiently perfect for not forming pinholes.

Moreover, the carrier structure and the electrolyte may according to the invention be manufactured directly atop one another without involving an assembling process prior to the sintering, and a contraction-controlling substance may have been added to said carrier structure. The contraction-controlling substance may, if desired, be formed by a sintering-promoting substance, such as Mn in an amount of 0.05 to 25 metal atom%, preferably 0.05 to 10 metal atom% and especially 0.1 to 5 metal atom% in order to obtain a sufficient, uniform sintering shrinkage of the carrier structure and the electrolyte.

Brief Description of the Drawings

The invention is explained in greater detail below with reference to the accompanying drawings, in which

15 fig. 1 is a cross sectional view of a carrier structure with an electrolyte applied thereon, viz. a so-called half-cell, and with and without a functional electrode layer,

Fig. 2 is a cross sectional view of an electrochemical cell including a half-cell, cf. Fig. 1, with a cathode applied thereon,

20 Fig. 3 is a cross sectional view of a set-up for an electrical characterization of an electrochemical cell with a platinum net applied onto the cathode surface and onto the surface of the carrier structure, said cell being mounted between some gas distribution plates which in turn are coupled between two sets of concentric aluminium pipes, gases being fed through the outer pipe and leaving through the inner pipes,

Fig. 4 illustrates two sets of measuring data, each set including area-adjusted cur-

rent-voltage curves, the DC resistance of the cell corresponding to the negative inclination,

Fig. 5 is a cross sectional view of a symmetrical measuring device with two identical carrier structures and two identical functional electrode layers and an intermediate electrolyte, where the measuring device is contacted between two platinum balls with their respective platinum conductors,

Fig. 6 shows measuring data in form of two impedance spectra after adjustment for electrode area and electrolyte resistance, where the squares correspond to carrier structures without air-entraining substances, and circles correspond to corresponding articles including 40% by volume of corn starch, viz. 9.5% by weight, in the carrier structure,

Fig. 7 shows an equivalent circuit for interpretation of the measuring data of Fig. 6, where L is inductance, R_s is a series resistance in the electrolyte, R_p is the polarisation resistance of the electrode, R_D is the diffusion resistance inside the carrier structure and outside said structure, and Q are constant phase elements representing a non-ideal capacitance associated with the said resistances,

Fig. 8 is a sectional view through the half-cell of Fig. 1 with metal plates glued thereon, said metals plates comprising towing eyes for a strength test in connection with a uniaxial pull,

Fig. 9 shows measuring data for the tensile strength of the half-cell at room temperature,

Fig. 10 shows dilatometric curves measured on cylinders of non-sintered sheets of a tape-cast electrolyte and carrier structure. The shrinkage of the articles during the sintering appears from the curves. 1) sheet of carrier structure without a

sintering-promoting substance, 2) sheet of carrier structure admixed 3.5 metal atom % MnO_2 as sintering-promoting substance, 3) sheet of electrolyte material.

Best Mode for Carrying Out the Invention

According to the invention a gasproof, thin electrolyte 1 is provided on the surface
5 of a porous carrier structure 3, cf. Fig. 1. Since the electrolyte layer 1 is made thin, the electric resistance in said layer is reduced and the efficiency of the completed half-cell is increased. It is also desired to maintain a predetermined thickness of the electrolyte 1 in such a manner that said electrolyte is totally tight during an industrial manufacturing. The thickness should furthermore be such that expectable pollutions
10 of the electrolyte 1 during operation do not cause a through electron conductivity and consequently a short-circuiting of the completed half-cell. Accordingly, attempts have been made at providing an industrial manufacturing technique rendering it possible to allow an electrolyte thickness of the magnitude 10 to 40 μm . As a result, it is also possible to obtain a predetermined material reduction and a predetermined reduction
15 of the production price.

The production price of the cell can be further reduced by minimizing the thickness of the carrier structure 3 because material reductions and reduced diffusion paths through the structure are obtained for the reacting gases. The latter should, however, be weighed or balanced against the total strength of the component, inter alia because
20 a predetermined porosity in the carrier structure 3 is desired.

Finally, it should be possible to manufacture a half-cell with the above properties by a cost-effective process due to addition of a sintering-promoting substance to the carrier structure 3 in order to avoid undesirable deformations during the sintering, if necessary.

25 The entire electrochemical cell is here in form of a fuel cell, such as an SOFC fuel

cell, and includes a gasproof electrolyte 1 surrounded by two porous electrodes, cf. Fig. 2. One electrode can operate as a carrier structure 3 for the cell or form part of said carrier structure. In the latter case, a functional electrode layer 4 is inserted between the carrier structure 3 and the electrolyte 1. cf. Fig. 1A. The functional
5 electrode layer 4 ensures an electrochemical conversion of reactants whereas the carrier structure 3 both reinforce the cell and operates as a current collector.

The cell is made of the following materials:

Carrier structure (anode): A mixture of NiO and yttrium-stabilized zirconia (YSZ), where NiO is reduced to Ni during operation of the fuel cell. MnO₂ is added as
10 sintering-promoting substance.

Functional electrode layer: A mixture of NiO and YSZ.

Electrolyte: YSZ.

Cathode: A mixture of lanthane strontium manganite (LSM) and YSZ.

Other materials can, however, also be involved. YSZ can as electrolyte for instance
15 be replaced by an oxygen-ionic conducting ZrO₂ doped with a combination of Sc, Y and other elements. The YSZ-fraction in the carrier structure 3 can, if desired, be replaced by another strength-providing material, such as Al₂O₃ or ZrO₂ or a combination thereof, optionally admixed one or more dopants. The layer dominating with respect to thickness in the carrier structure can, if desired, include ZrO₂, which has
20 been partially stabilized with other oxides to such an extent that martensitic phase transformation can occur at the handling and mounting temperatures of the cell. The stabilizing oxide can optionally be Y₂O₃ in an amount of 8 mol%, especially less than 5 mol%. Ni as electrically conducting material in the carrier structure can also be replaced by other electronic conductors. Other additives including Mn can be used

as sintering-promoting substance. In principle, the cathode 6 can also operate as the carrier structure.

The manufacture of a slip for moulding/spraying of the carrier structure 3 and the electrolyte 1, respectively, employs organic auxiliary materials:

- 5 Solvent: Ethanol or a mixture of ethanol and methylethylketone

Dispersant: Polyvinylpyrrolidone

Binder: Polyvinyl butyral

Softener: Polyethylene glycol and/or dibutylphthalate

Slip: Additol sold by Vianova Resins (Trade name)

- 10 Air-entraining substances: Corn starch or a surplus of the above organic auxiliary materials.

These auxiliary materials can, however, be replaced by other materials decomposing or oxidizing during the sintering without leaving substances detrimental to the properties of the structure.

- 15 Two methods of manufacture are described below:

I. Tape casting of the electrolyte 1 followed by a spraying of the functional electrode layer 4 and a tape casting of the carrying cell structure 3.

For manufacturing the electrolyte, the electrolyte material is suspended in a solvent. Organic auxiliary materials are added, such as a dispersant, a binder, a softener and

a slip. The suspension is subjected to a ball grinding. The slip is evacuated and subjected to a filtering prior to the moulding. Slips for the manufacturing of the carrier structure and for the spraying of the functional electrode layer, respectively, are manufactured in a similar manner.

- 5 The electrolyte slip is cast on a carrier substrate, viz. a silicon-coated Mylar sheet. Other sheets can, however, also be involved in connection with the tape casting. Upon the drying of the manufactured sheet, the functional electrode layer is sprayed onto the electrolyte sheet. Subsequently, the carrier structure of the cell is manufactured on the electrolyte sheet with the functional layer 4. Upon the drying, articles
10 are cut out in desired sizes for sintering.

II. Tape casting of the carrier structure 3 followed by an airborne spraying of the functional electrode layer 4 and the electrolyte 1.

- A slip for manufacturing the carrier structure 3 of the cell is manufactured as described under I. The slip is moulded on a carrier substrate 3, viz. a silicon-coated
15 Mylar sheet, whereafter the sheet is dried. Other sheets can, however, also be involved. The slip for the airborne spraying of the functional electrode layer 4 and the electrolyte is manufactured as described under I. The functional electrode layer 4 is sprayed onto the cast carrier structure sheet either before or after the cutting of the sheet. After the drying, the electrolyte is sprayed thereon, and the cut out articles are
20 subjected to a sintering.

Both manufacturing methods involve a sintering of the articles at 1250 to 1400°C, typically at 1300°C for 12 hours. During the sintering, the articles are typically placed on a porous ceramic support, and they can, if desired, be covered by a corresponding plate.

25

By both manufacturing methods, the sheet moulding can in principle be replaced by

methods such as serigraphy, rolling or extrusion, whereas the airborne spraying can be replaced by for instance serigraphy, electrostatic spraying, swabbing or immersion.

By both manufacturing methods a functional electrode layer can, if desired, be omitted between the carrier structure 3 and the electrolyte 1.

The slip for manufacturing the carrying cell structure can, if desired, be admixed a sintering-promoting substance, such as MnO_2 , in order to adjust the sintering shrinkage to the shrinkage of the electrolyte. Mn or MnO_2 can advantageously be added in amounts of from 0.05 to 25 metal atom%, preferably 0.05 to 10 metal atom% and especially 0.1 to 5 metal atom% to the carrier structure in order to obtain a uniform sintering shrinkage of the carrier structure and the electrolyte. In addition, the shrinkage and the porosity of the carrier structure can be adjusted by a suitable calcination and crushing of the materials forming part of the carrier structure, and by an addition of organic auxiliary materials or air-entraining substances.

Square articles were manufactured with the dimensions of up to 12 times 12 cm^2 as well as round articles of a diameter of 12 cm. A scaling from 5 times 5 cm^2 to 12 times 12 cm^2 involved no particular problems, and further scalings are possible.

The described methods can be used directly for mass production.

The half-cell according to the invention is manufactured by cost-effective procedures as the ceramic techniques used are simple and scalable. No cost-intensifying additional operations for assembling the carrier structure and the electrolyte are involved. The carrier structure, the electrolyte and an optionally functional electrode layer are sintered together, which reduces the number of sintering steps compared to a separate sintering of each element. The thickness of the carrying electrode structure is less than 700 μm , preferably less than 500 μm , especially less than 300 μm . The thick-

ness of the electrolyte is between 10 and 40 μm , preferably between 10 and 25 μm , especially between 15 and 25 μm .

The carrier structure is made thin and porous while maintaining the necessary strength and a suitable electrolyte thickness. An advantage is thus obtained because
5 the efficiency restrictions caused by the gas diffusion in the carrier structure are minimized.

Examples of embodiments

Example I

A fuel cell is manufactured with an electrolyte shaped by way of sheet moulding of
10 YSZ with 8 mol% Y_2O_3 . A functional electrode layer is applied onto the cell, said electrode layer including 56% by weight of NiO and 44% by weight of YSZ with 8 mol% Y_2O_3 by means of an airborne spraying. The carrier structure includes 56% by weight of NiO and 44 by weight of YSZ with 3 mol% Y_2O_3 , to which 3.5 metal atom% of MnO_2 are added as sintering-promoting substance. The carrier structure
15 is sheet moulded onto the functional layer.

The component including the electrolyte, the functional layer and the carrier structure is punched out. The component is sintered between two porous ceramic plates at 1300°C for 12 hours. Subsequently, the thickness of the carrier structure, the functional anode layer and the electrolyte is approximately 200 μm , 10 μm and 15
20 μm , respectively.

Then a cathode with a functional layer of LSM and YSZ as well as a current-collecting layer of LSM is applied by way of airborne spraying and sintered at 1100°C for two hours.

The efficiency of the cell is characterised as follows, cf. Fig. 3.

- Circular, woven Pt grids of an area of 5.7 or 7 cm² are mounted on the cathode surface and the surface of the carrier structure.

- 5 As a result, the cell has been efficiently contacted where it is covered by the platinum grid.

The cell with the contacting is mounted between two plane gas distribution plates 10 with openings and ribs which ensure gas access to the electrodes. The cell and the contacting and the gas distribution plates 10 are mounted between two sets of alumina
10 pipes 11, 12 in an oven, cf. Fig. 3. The cell is heated to a temperature of 1050°C. The temperature is measured by means of thermocouples arranged 1 mm above the centre of the cell.

The cathode side is fed with air, whereas the anode side is fed with hydrogen moistened with 2% water. The gases are fed through the outer pipes 11 and removed
15 through the inner pipes 12. The voltage across the cell can be measured at the edge V_K and the centre V_C of the electrodes. Current is collected on the cell through the platinum grids and separate conduits by loading with external resistances, and current-voltage curves, cf. Fig. 4, are taken at the edge and the centre, respectively. The negative inclination of the current-voltage curves correspond to the DC resistance of
20 the cell. Considering the entire measured range, an area-specific internal resistance of 0.42 Ωcm^2 is obtained at 860°C with hydrogen saturated with 2% water and air on the anode and the cathode side, respectively. The cell voltage in the unloaded state corresponds to the theoretical voltage between the present gases at the operational temperature, which shows that the electrolyte is gasproof.

- 25 The completed article is strong and flexible. The latter can be illustrated by a loss of less than 10% being determined during the sintering and the handling of the sintered

article, which includes the carrier structure and the electrolyte, said loss being determined during the further manufacture of the cell. Such a loss is very small compared to typical losses during the manufacture of composite ceramic components.

The gas density of the electrolyte is verified by application of a colour penetrant (diamant fuchsine) and a redrying thereof, which in case of sintering errors or pores is absorbed and leaves a distinct discoloration.

Example II

A fuel cell is manufactured by way of sheet moulding or tape casting of a carrier structure including 56% by weight of NiO and 44% by weight of YSZ with 3 mol% of Y_2O_3 , which has been admixed 3.5 metal atom% of MnO_2 as sintering-promoting substance. After the punching out of the carrier structure, a functional electrode layer including 56% by weight of NiO and 44% by weight of YSZ with 8 mol% of Y_2O_3 is applied by way of airborne spraying. An electrolyte of YSZ with 8 mol% of Y_2O_3 is sprayed thereon.

Then the half-cell is sintered between two porous ceramic plates at 1300°C for 12 hours. Subsequently, the thickness of the carrier structure, the functional anode layer and the electrolyte is approximately 200 μm , 10 μm and 15 μm , respectively.

Then a cathode with a functional layer of LSM and YSZ as well as a current-collecting layer of LSM is applied onto the electrolyte by way of airborne spraying and sintered at 1100°C for two hours.

Measured in the same manner as in Example I, an area-specific internal resistance of 0.40 Ωcm^2 is obtained at 890°C with hydrogen 2% water and air on the anode and the cathode side, respectively. The cell voltage in the unloaded state corresponds to the theoretical voltage between the present gases at the operational temperature,

which shows that the electrolyte is gasproof.

Exactly the same manufacture and test are carried out on a cell, where 40% by volume of corn starch is added to the slip forming the carrier structure.

The completed article is strong and flexible. The latter can be illustrated by a loss of less than 10% being determined during the sintering and the handling of the sintered article, which includes the carrier structure and the electrolyte, said loss being determined during the further manufacture of the cell. Such a loss is very small compared to typical losses during the manufacture of composite ceramic components.

The gas density of the electrolyte is verified by application of a colour penetrant (diamant fuchsine) and a redrying thereof, which in case of sintering errors or pores is absorbed and leaves a distinct discoloration.

Sintering properties

Separated sheets of slip for the manufacture of carrier structure and electrolyte are in both cases manufactured by way of sheet moulding. The sintering properties of these sheets is tested by rolling said sheets into cylinders and by carrying out measurements in a dilatometer. The measuring curves of Fig. 10 show how the sheets are compacted during the sintering. By comparing the curves 1) and 2), the increased sintering shrinkage appears by addition of the contraction-promoting substance MnO_2 for the carrier structure. The sintering shrinkage of the electrolyte appears from curve 3). A suitable addition of MnO_2 and other measures changing the sintering shrinkage of the carrier structure render it possible to adjust the shrinkage of the carrier structure to the sintering shrinkage of the electrolyte. A distinct difference exists in the sintering properties of the electrolyte sheet and the carrier structure sheet, but as the same total shrinkage is obtained at the final temperature, plane articles are obtained without deformations after cooling. The latter is difficult to

obtain without adding a sintering-promoting substance, such as Mn. The requirement to the same shrinkage is significantly increased at a scaling of the size of the sintered article.

Diffusion resistance in the carrier structure

5 Yet another functional electrode layer as described in Example 1 is sprayed onto a non-sintered article as described in Example I, and yet another carrier structure is sheet moulded as described in the Example. This symmetrical article is punched out in a size of $5 \times 5 \text{ mm}^2$ and subjected to a sintering at 1300°C for 12 hours. The edges of the article are subjected to a grinding so as to ensure that short-circuits do not
10 occur across the edge of the electrolyte layer 1, cf. Fig. 1. The manufactured cells are mounted between four platinum wires 6 arranged such that two are positioned on the central portion of each electrode surface, cf. Fig. 5. The cells are placed in an oven in a controlled atmosphere of hydrogen moistured with 3% water. The impedance of the cells is measured by impedance spectroscopy at 850°C . The measuring
15 data are indicated as squares in Fig. 6.

A curve fitting of the impedance measurements was performed by means of the program "Equivalent Circuit", with an equivalent circuit being adjusted to the measured data of Fig. 6. The equivalent circuit includes capacitances C, inductances L,
20 resistances R and constant phase elements Q.

The equivalent circuit used for the curve fitting is shown in Fig. 7, where L is an induction also covering phase errors in the measuring equipment at high frequencies, R_s is a series resistance including a resistance substantially in the electrolyte, R_p & Q_p represent limiting steps in the electrode reaction, whereas R_D & Q_D represents the
25 gas phase diffusion resistance inside the carrier structure and outside the structure. An R_p of approximately $90 \text{ m } \Omega\text{cm}^2$ and an R_D of approximately $150 \text{ m } \Omega\text{cm}^2$ are obtained.

Exactly the same manufacture and test are carried out on a symmetrical article, where, however, 40% by volume of corn starch is added to the slip forming the carrier structure. As illustrated in the impedance measurements, viz. the circles cf. Fig. 6, a distinct difference applies to the resistance R_D relating to the width of the characteristic curve shown to the very right. An R_p of approximately $60 \text{ m } \Omega \text{ cm}^2$ and an R_D of approximately $80 \text{ m } \Omega \text{ cm}^2$ are obtained. The entire change in R_D can be ascribed to the increase of the porosity caused by the corn starch, whereas a substantial portion of the remaining R_D can be ascribed to stagnant gas outside the carrier structure in the test set-up. By adding an air-entraining substance providing an increased porosity it is thus possible to obtain an improved diffusion and consequently an improved efficiency of the completed cell.

The strength of the cells is particularly important during the handling following the sintering, during the application of the cathode as well as during the assembling of the cells into a stack of cells. In all these situations and up to the reduction of the carrier structure during the operationalization, the strength of the cell is dictated directly by the properties of the half-cell. Half-cells in the dimensions $1 \times 9 \text{ cm}^2$ are manufactured as described under I. These articles are connected by metal plates glued thereon and provided with towing eyes 8 at both ends, cf. Fig. 8. These towing eyes are subjected to a uniaxial pull in a traction machine until they break, and the fracture strength is standardized towards the dimensions of the article perpendicular to the longitudinal axis at the breaking location. The strength is indicated in a so-called Weibull plot, cf. Fig. 9.

The electrolyte surface can optionally be micro-corrugated or rough in order to increase the surface and improve the physical adhesion of an electrode. The half-cell, viz. the carrier structure, optionally the electrode structure and the electrolyte, can be corrugated so as to be able to tolerate temperature gradients across the extension of the cell.

Claims

1. Electrochemical cell, such as a fuel cell, comprising a porous, carrying electrode structure, optionally including several layers, on which an electrolyte and yet another electrode are deposited, where the carrying electrode structure and the electrolyte are
5 sintered together, for instance an Ni/YSZ anode including several layers and where an YSZ electrolyte and a cathode are deposited thereon, c h a r a c t e r i s e d in that the carrying electrode structure (3) and the electrolyte (1) are manufactured directly atop one another without involving an assembling process prior to the sintering, and that the thickness of the carrying electrode structure is less than 700 μm ,
10 preferably less than 500 μm , especially less than 300 μm , and that the thickness of the electrolyte positioned thereon is between 10 and 40 μm , preferably between 10 and 25 μm and especially between 15 and 25 μm , and that a contraction-controlling substance can be added to the carrying electrode structure.
2. Electrochemical cell as claimed in claim 1, where the contraction-controlling
15 substance is Mn in an amount of from 0.05 to 25 metal atom%, preferably 0.05 to 10 metal atom% and especially 0.1 to 5 metal atom% added to the carrier structure in order to obtain a uniform sintering shrinkage of said carrier structure and the electrolyte.
3. Electrochemical cell as claimed in claim 1 or 2, where the layer dominating with
20 respect to thickness in the carrier structure include ZrO_2 which has been partially stabilized with other oxides to such an extent that martensitic phase transformation can occur at the handling and mounting temperatures of the cell.
4. Electrochemical cell as claimed in claim 3, where the stabilizing oxide is Y_2O_3 in amounts of preferably less than 8 mol%, especially less than 5 mol%.
- 25 5. Electrochemical cell as claimed in claim 1 or 2, where the carrying electrode

structure is manufactured by tape casting, and where the electrolyte structure and an optional intermediate electrode structure are manufactured by airborne spraying or the like cost-effective scalable processes.

6. Electrochemical cell as claimed in claim 1 or 2, where the electrolyte structure and
5 the carrying electrode structure are manufactured by tape casting, and where a possible intermediate electrode structure is manufactured by airborne spraying or the like cost-effective scalable processes.

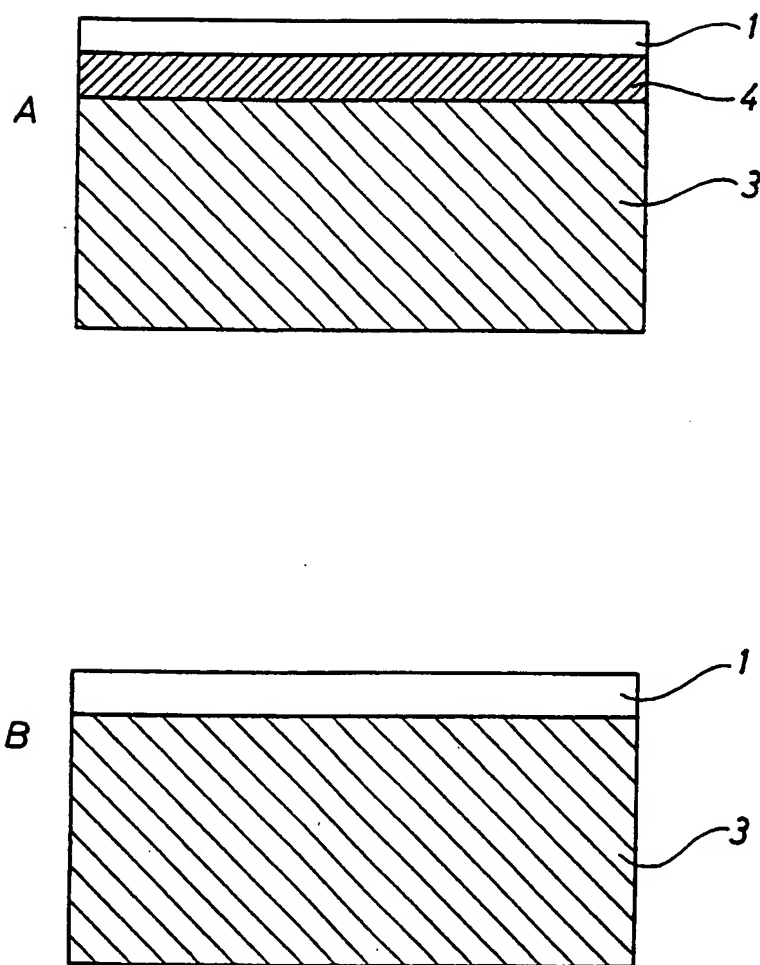


Fig. 1

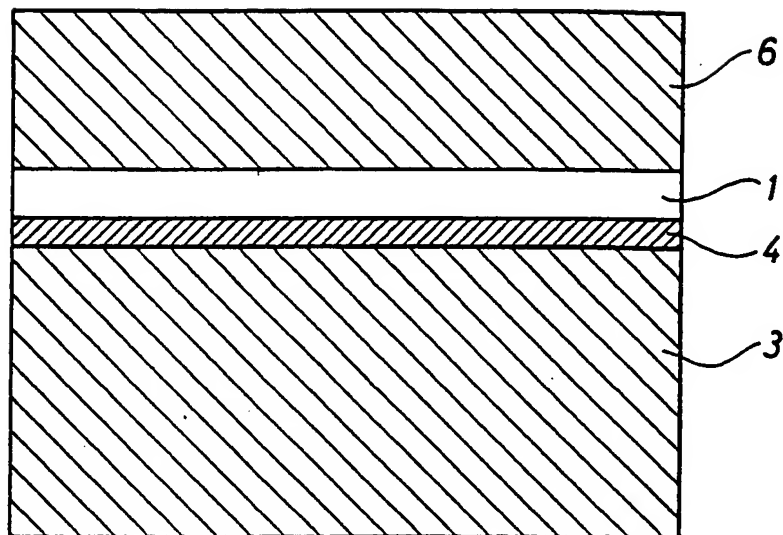
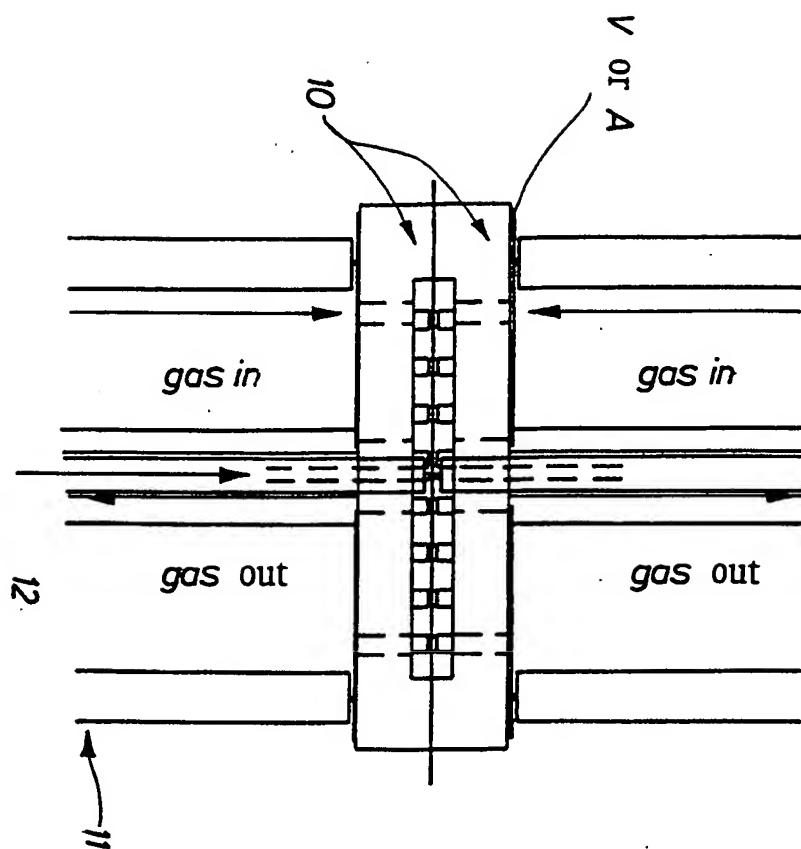


Fig. 2

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**Fig. 3**

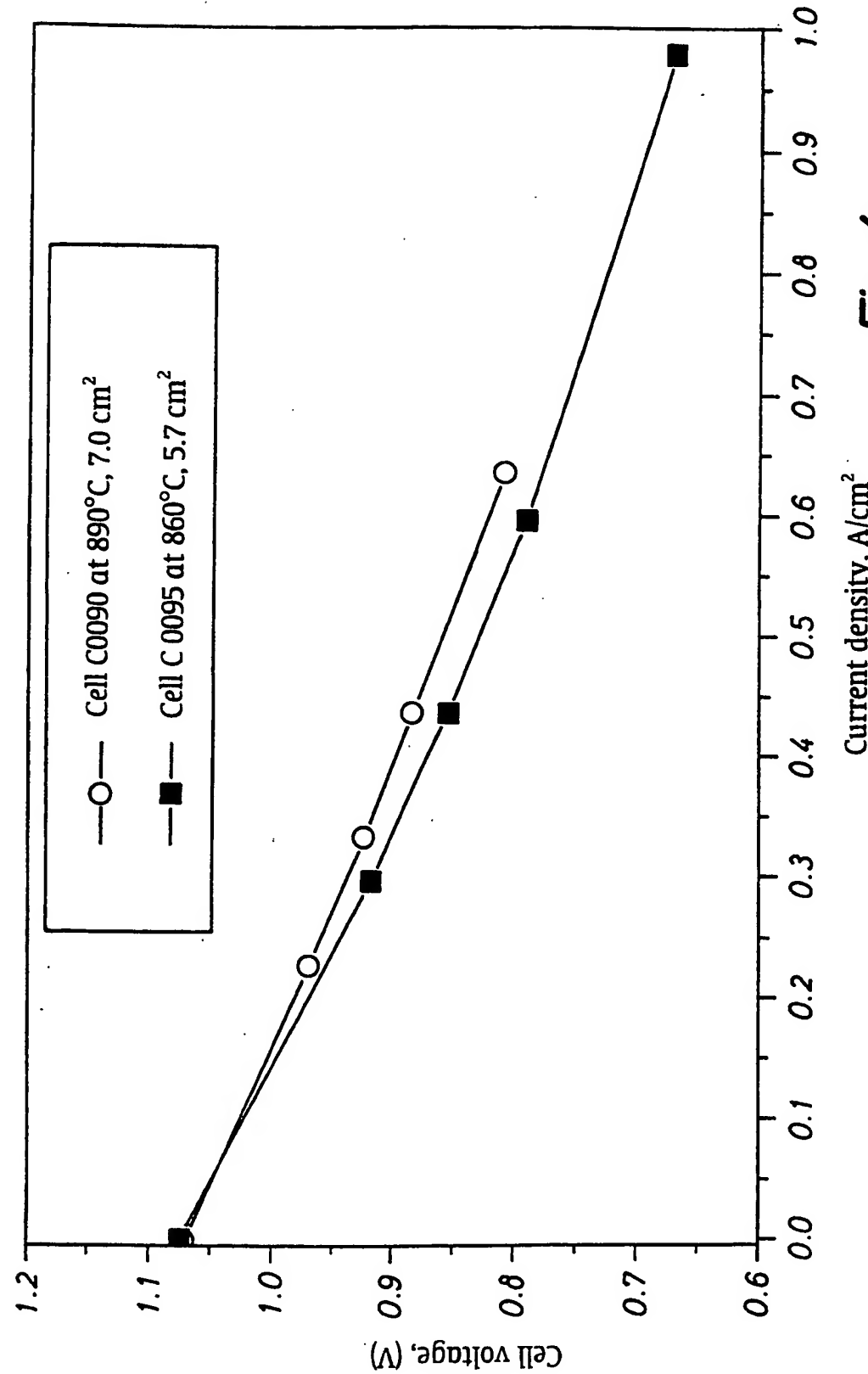


Fig. 4

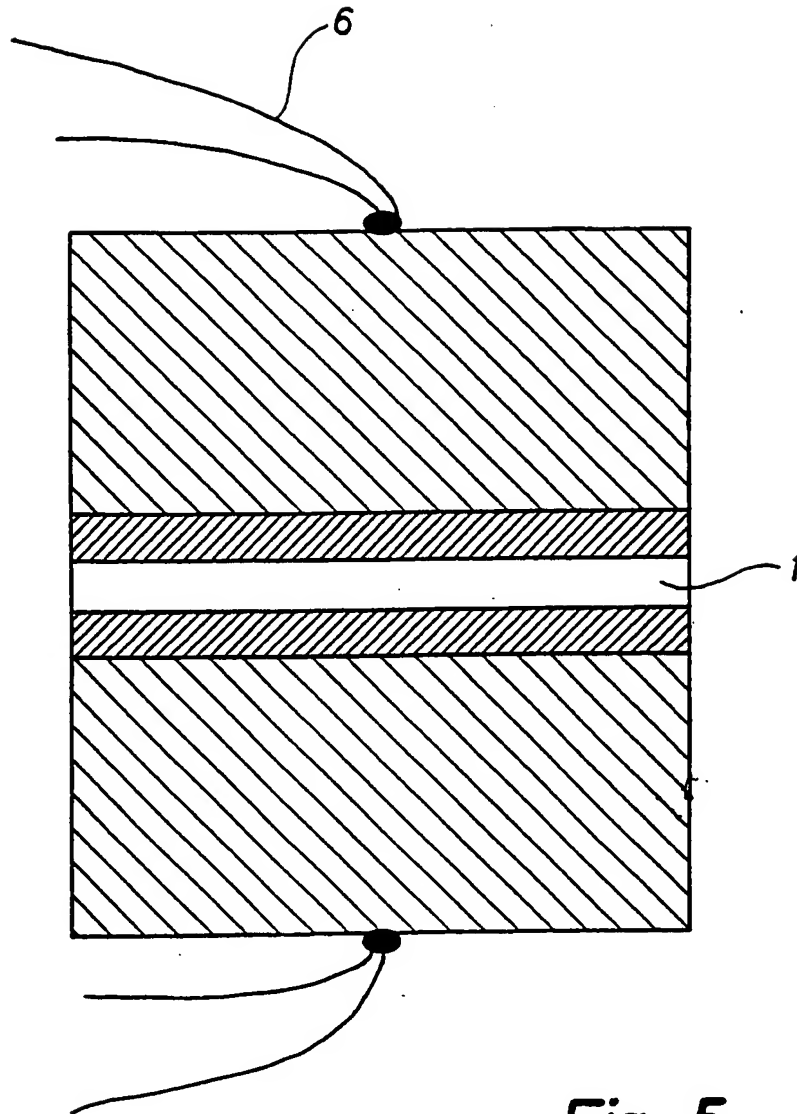


Fig. 5

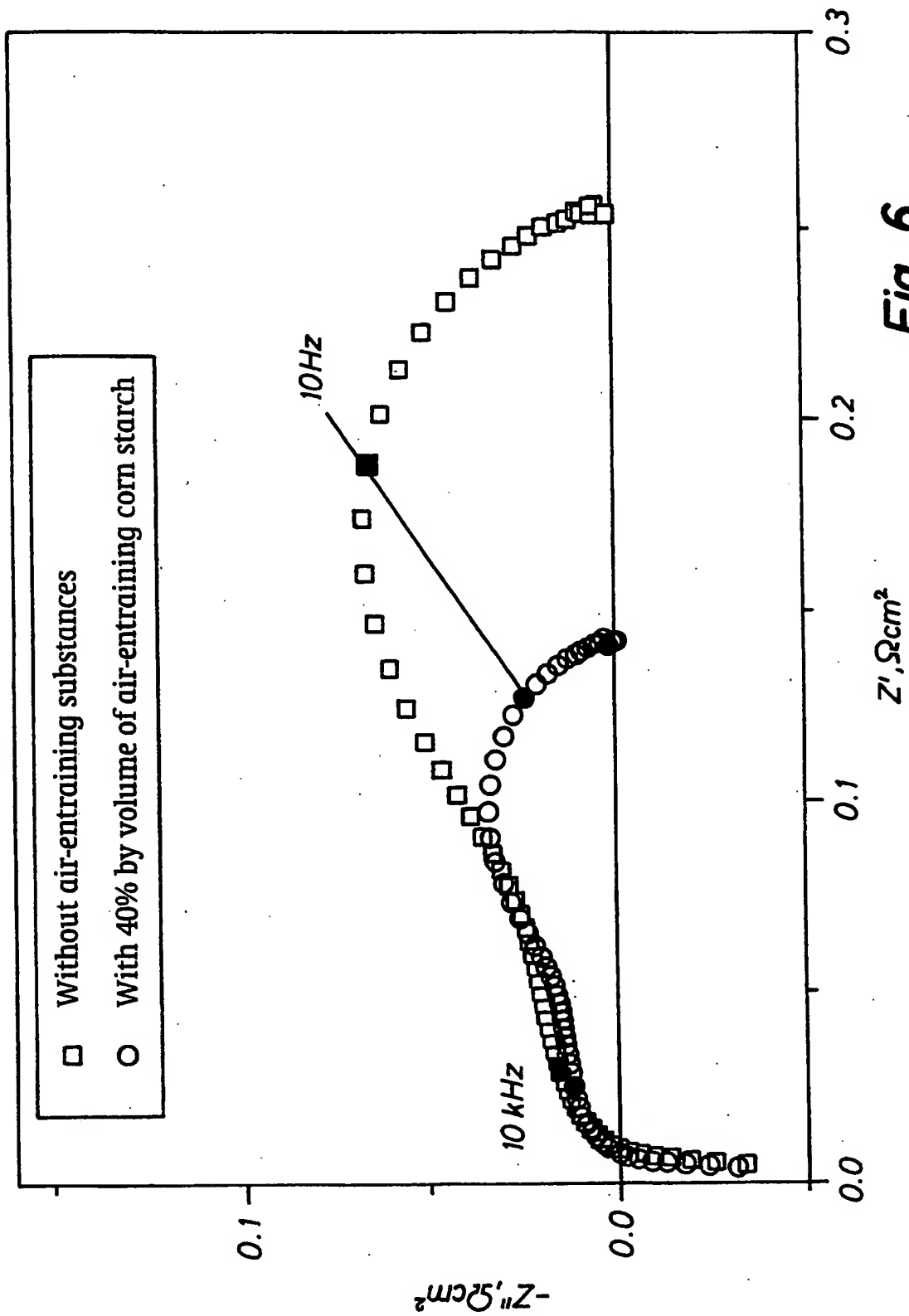
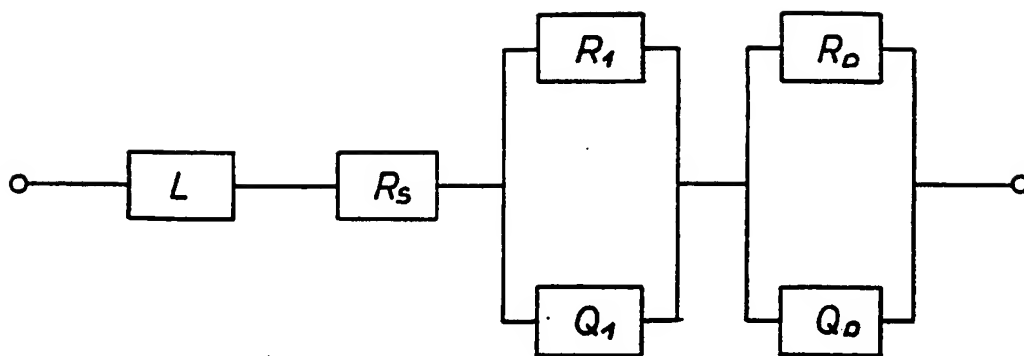


Fig. 6

***Fig. 7***

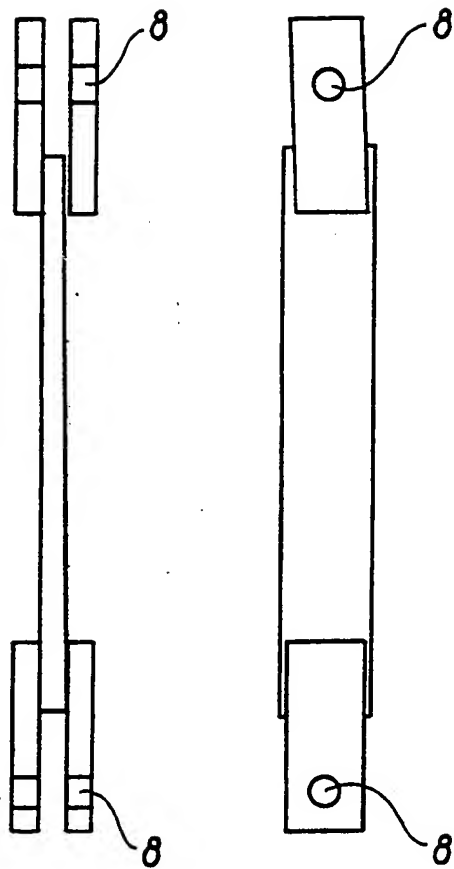


Fig. 8

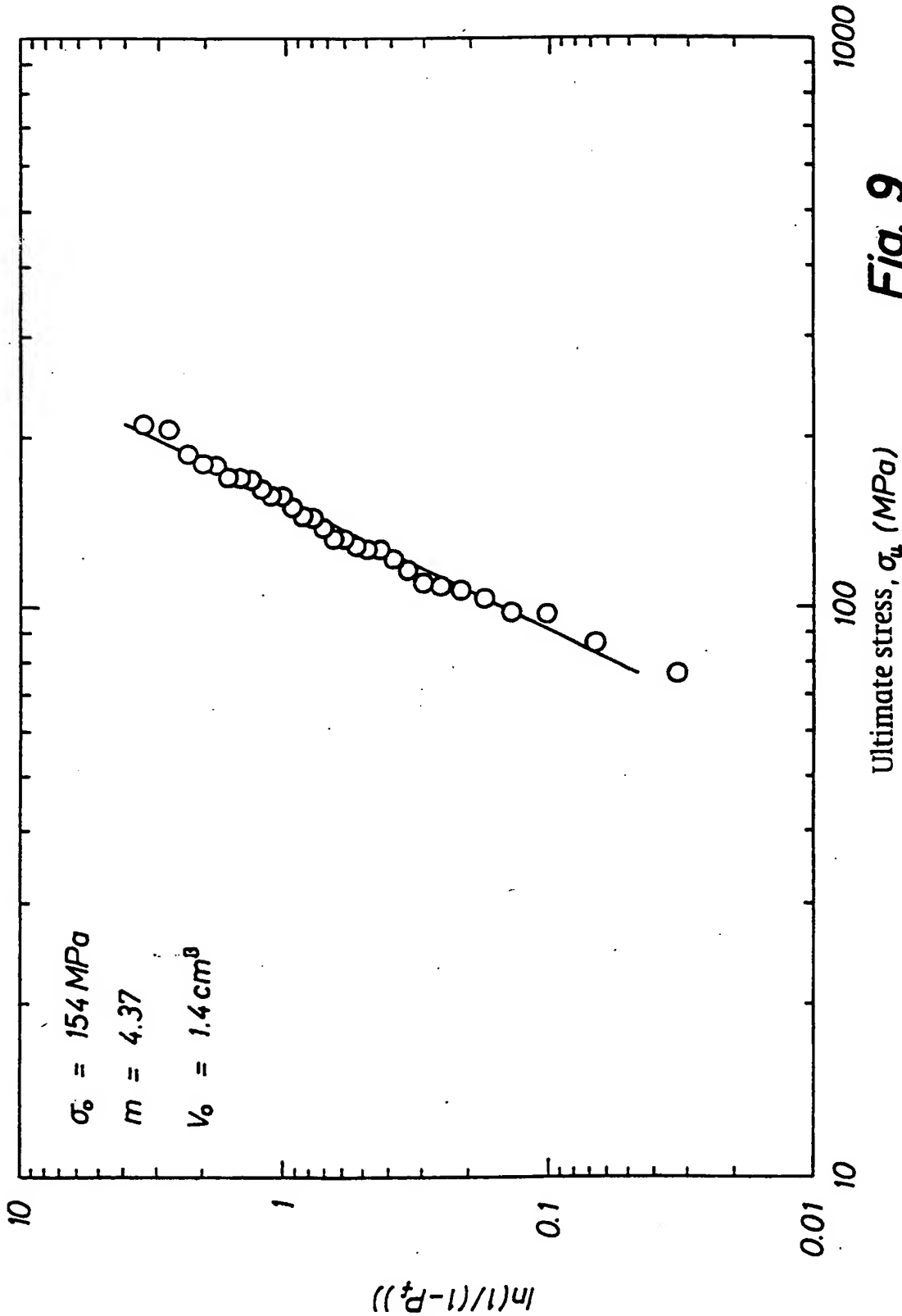
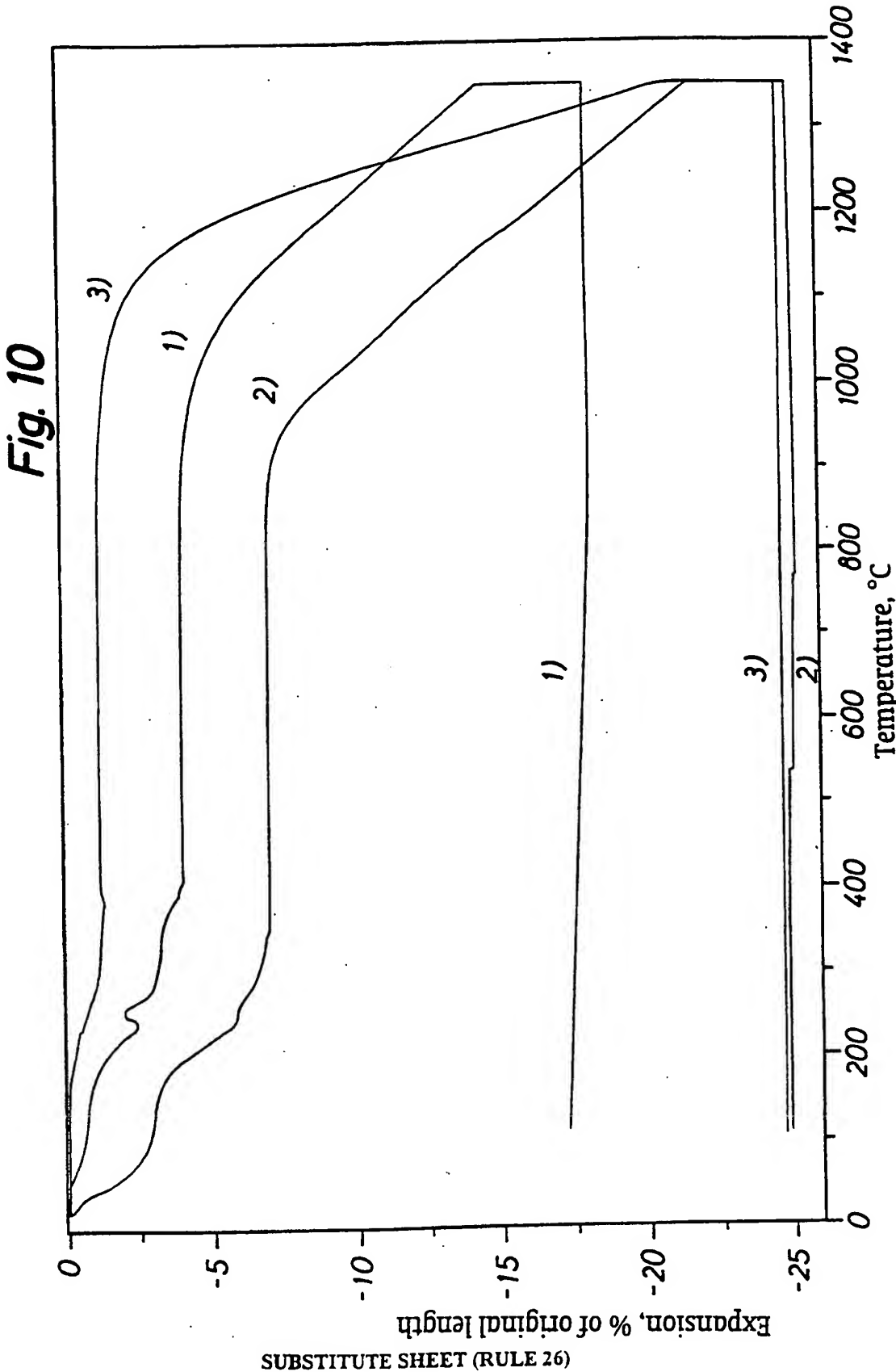


Fig. 9



INTERNATIONAL SEARCH REPORT

International Application No

PCT/DK 00/00228

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 H01M4/88 H01M8/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 199836 Derwent Publications Ltd., London, GB; Class L03, AN 1998-424008 XP002901109 & JP 10 177862 A (MITSUBISHI JUKOGYO KK), 30 June 1998 (1998-06-30) abstract</p>	1
A	<p>EP 0 714 104 A (TOTO LTD) 29 May 1996 (1996-05-29) page 2, line 8 - line 51 page 3, line 23 - line 31</p> <p style="text-align: center;">--- -/- ---</p>	1-6



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

17 July 2000

Date of mailing of the international search report

29.08.00

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U. Granlund/MP

INTERNATIONAL SEARCH REPORT

International Application No

PCT/DK 00/00228

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 199551 Derwent Publications Ltd., London, GB; Class L02, AN 1995-400799 XP002901110 & JP 07 277848 A (NGK INSULATORS LTD), 24 October 1995 (1995-10-24) abstract</p> <p style="text-align: center;">---</p>	2
A	<p>PATENT ABSTRACTS OF JAPAN vol. 015, no. 086 (E-1039), 28 February 1991 (1991-02-28) & JP 02 301966 A (MATSUSHITA ELECTRIC IND CO LTD), 14 December 1990 (1990-12-14) abstract</p> <p style="text-align: center;">-----</p>	5,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/DK 00/00228

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 10177862 A	30-06-1998	NONE	
EP 0714104 A	29-05-1996	US 5968673 A CA 2163267 A WO 9526031 A	19-10-1999 28-09-1995 28-09-1995
JP 7277848 A	24-10-1995	NONE	
JP 02301966 A	14-12-1990	NONE	